

**PROCESS FOR REDUCING THE BIURET CONTENT IN UREA**

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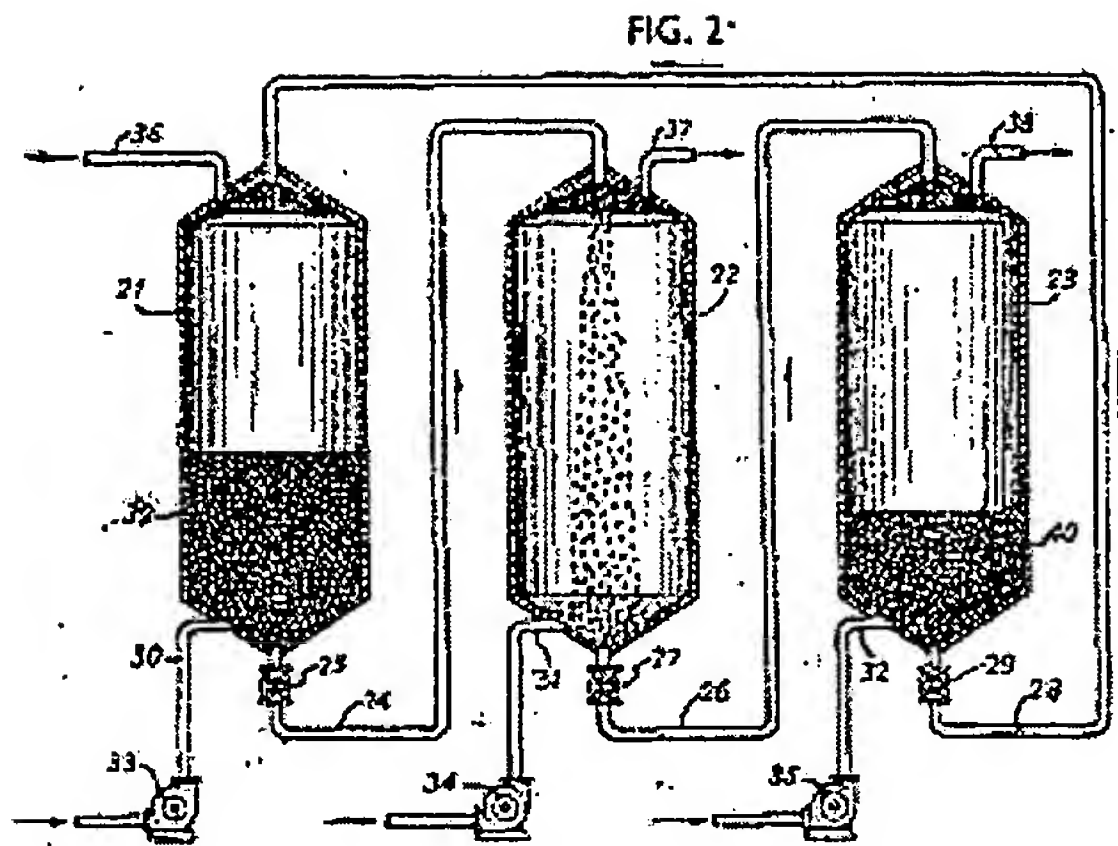
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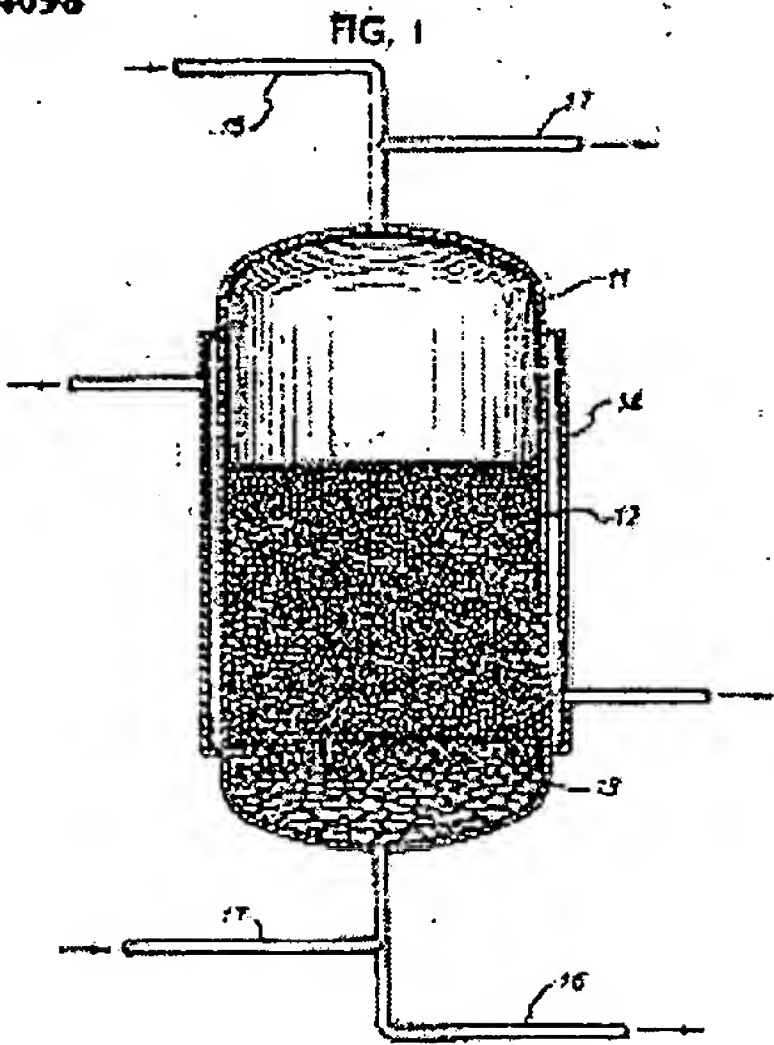
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1404098 Ion-exchange GUANOS Y FERTILIZANTES DE MEXICO SA 16 May 1973  
23272/73 Heading B1J [Also in Division C2] An apparatus suitable for the purification of urea by contacting it with an ion-exchange resin in a batch process comprises a column 11, containing the resin 12 supported on graded sand 13, surrounded by a steam jacket 14 and provided with inlet and outlet lines 15 and 16 respectively. The lines 15 and 16 are provided with lines 17 for introducing backwash liquid at the lower end of the column and removing some from the upper end. An apparatus suitable for the continuous purification of urea comprises three columns 21, 22, and 23 provided at their lower ends with inlets 30, 31 and 32 respectively and at their upper ends with outlets 36, 37 and 38 respectively. The lower ends of columns 21, 22 and 23 are connected via lines 24, 26 and 28 respectively to the upper parts of columns 22, 23 and 21 respectively so that partially exhausted resin can be regenerated, and recycled. For Figure see next page



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## PATENT SPECIFICATION

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                   MARIN



## (54) PROCESS FOR REDUCING THE BIURET CONTENT IN UREA

(71) We, GUANOS Y FERTILIZANTES DE MEXICO, S.A., a Mexican Company organised according to the laws of Mexico of Avenue Insurgentes Sur 1079, Mexico 18, D.F., Mexico, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

5 The present invention relates to a process for treating a urea melt or solution containing biuret or a metal complex thereof to reduce the amount of biuret or complex thereof.

10 Heretofore a serious problem encountered in the manufacture of urea has been the biuret content in the end product. Biuret is an impurity of urea and it is a condensation product thereof, produced according to the following reaction:



The formation of biuret is a direct function of the temperature and the retention time; therefore, high temperatures and long retention times are avoided in all processes used. However, in order to obtain prilled urea, the most common form found on the market, it is necessary to use a sufficiently concentrated and fluid urea solution that allows the formation of a prill with such a moisture content that it prevents the caking of the stored and/or packed product. In order to obtain a solution capable of being prilled, it is necessary to operate at high temperatures. Besides this, the end product is reprocessed and subjected once more to the heating necessary for prilling and thus the biuret content increases again.

35 Urea is mainly used as an agricultural fertilizer, and in one of its forms is dispersed on the foliage of growing plants; and in such an event the biuret is extremely noxious since it possesses a very active phytotoxic action. Therefore, in order to produce a foliar grade

urea, that is, so that its solutions be dispersable on the leaves of the plants, it is necessary that it has a maximum biuret content of 0.2% by weight.

In addition to the above mentioned use, urea has a great variety of different usages in which a requisite is a low biuret content. One of these usages is, for example, the employment of urea in the production of synthetic resins and plastics. Likewise, a small amount of urea is used in pharmaceutical products and, logically, for this usage there is a serious restriction in the allowable content of biuret and other impurities. Also urea is used in solutions for textile treating and finishing. In this event, the biuret contained in the urea, together with the formaldehyde necessary for the textile treating, causes turbidity in the solutions and consequently it destroys the brilliancy of the textile finish, this being totally undesirable.

The usual process of manufacturing urea consists of contacting ammonia and carbon dioxide at high pressures and temperatures in a closed system. In this manner initially ammonia and carbon dioxide are exothermically combined forming ammonium carbamate which, under the reaction conditions, is partially converted into urea and water. Subsequently, the resulting urea, ammonium carbamate, ammonia and water are treated by different processes in order to recover the ammonia and the carbon dioxide. Finally, the water is evaporated to obtain a relatively pure concentrated urea solution, which is subjected to a suitable process in order to obtain the desired final form of urea, for example, prilled urea. In this last step and according to the aforementioned comments made in respect to the heating, it is not possible to avoid an undesirable percentage of biuret content in the end product.

Various methods have been proposed of avoiding the formation of biuret. For example,

a proposal was to mount the evaporator unit, which is generally used, on the top of the prilling tower so as to immediately transfer the urea melt to the prilling operation. This process is disadvantageous since it requires special supports for the evaporator, as well as extra lines for the steam and condensate.

Another process proposed as a solution to the problem of the biuret formation, consisted of ammoniation of the solutions containing biuret to split the biuret molecule thus reforming urea. This process requires high pressures during a substantial period and, therefore, it is inconvenient and the equipment costs make it uneconomic.

Another process for solving the problem of biuret formation in urea consisted of a partial crystallization of urea from its saturated solutions in order to provide relatively pure urea crystals, leaving most of the biuret in the mother liquors, and of a further reprocessing of the mother liquors through the reactor. However, this process has not yielded satisfactory results due to the fact that the recirculation of the mother liquors reduces the capacity of the urea plant and besides, the occlusion of biuret in the final urea crystals is not prevented.

Another process for the production of urea having a low biuret content consists of evaporating ammonia, carbon dioxide and a certain amount of water and passing them rapidly through an externally heated tube. Then, the liquid and gas mixture evolving from the tube was processed to separate the gas from the liquid; and subsequently the liquid was passed through a packed tower in countercurrent flow to a stream of hot air, thereby providing a final drying of the urea. This final drying could be replaced by the steps of crystallization and separation of crystals in a centrifuge. This process did not provide adequate results due to the several disadvantages it involves. That is, there was a premature crystallization resulting in clogging of the apparatus; the amount of decomposition products including biuret in the urea substantially increases due to the long time required by the high temperature evaporation; a high water content was found in the resulting product, therefore a subsequent drying step was required involving a consequent decomposition; there were losses of the desired product due to decomposition and the resulting granules of the end product were either larger or smaller than the required size.

Finally, some other processes for solving the problem of the biuret contents have been proposed, for example, one of them involves treating solid urea with a liquid solvent containing acetone to extract biuret from the solid urea and others only involve variations in operating pressures and temperatures or applying different crystallization conditions. Nevertheless these methods have not provided a suit-

able and efficient solution to the problem of biuret content in urea. 65

It is an object of the invention to provide an improved process for reducing the biuret content in urea.

According to the present invention we provide a process for treating a urea melt or urea solution containing 1.0 to 99.9% by weight of urea and an amount of biuret itself or a metal complex thereof to reduce the amount of biuret or complex thereof which comprises contacting the urea melt or solution with an ion-exchanging resin. For instance, an aqueous urea solution may be treated with the ion-exchanging resin. The process may be conducted at a temperature of 0°C to 200°C. 70

With reference to the accompanying drawings, Figure 1 is a schematic sectional view illustrating an embodiment of an ion-exchange system employable with the present invention, and 75

Figure 2 is a schematic view illustrating another embodiment of an ion-exchange system employable with the present invention.

The type of the ion-exchanger is not critical since any type work. However, ion-exchangers capable of regeneration and operating at high temperatures (200°C.) are preferred; and of these ion-exchange resins of a strong base anionic type are especially preferred. 80

Once the ion-exchange operation has been carried out and the biuret has been separated from the urea, the biuret may be displaced from the resin by any stronger anion, for example, bicarbonates, carbonates, chlorides, nitrates, sulphates and hydroxides. Nevertheless the preferred ones are the hydroxides because they are the only anions that totally displace the biuret, leaving the resin in a condition capable of again retaining the biuret. 85

The aforementioned ion-exchange can be carried out through a column containing a suitably supported ion-exchange resin. 90

In one of the embodiments of the present invention (see Figure 1 of the accompanying drawings) a column contains a strongly basic resin 12, for example, of the styrene type. The resin 12 is supported by means of graded sand 13 providing an adequate support, for avoiding loss of the resin 12 during the ion-exchange operation. The column 11 is provided with a surrounding jacket 14 through which low pressure steam passes for maintaining the required temperature, in order to avoid solidification of urea. 95

The volume of column 11 must be such as to include the graded sand 13 and the ion-exchanging resin 12 and to allow a clearance corresponding to 75% of the volume of resin 12 to minimise loss of same during the processing operations. 100

In this type of ion-exchanger, the feeding of the urea melt or urea solution to be treated is carried out through an upper line 15, in- 105 110 115 120 125



cluding its corresponding distributor (not shown), in order to immediately contact the urea to be treated with the ion-exchanging resin 12. Once the urea is processed it discharges from column 11 through a lower line 16.

The regeneration and rinse of the ion-exchanging resin 12 are carried out likewise through lines 15 and 16. However, since a backwash is necessary, lines 17 are included for introducing the backwashing liquid at the lower end of the column 11 and removing same through the upper end.

The process for reducing the biuret content in a urea solution in this type of apparatus can be carried out in the following manner:

Water necessary for keeping the resin 12 fully covered, is partly drained until it is just above the level of the resin 12, so as to prevent dilution of the urea solution and to avoid modification in the ion-exchange operation by air bubbles due to excess drainage. The urea solution is fed through line 15 to column 11, thereby displacing the water retained in the ion-exchange resin 12 which water flows through line 16. Consequently, the liquid in the effluent at this time is essentially water, therefore it is eliminated through line 16 until the said liquid is an urea solution with concentration of 4 to 5% by weight of urea, then the outflowing urea solution, which is a biuret free urea solution, is recovered as an end product. This operation is maintained until, by means of a qualitative test, biuret is detected in the effluent; the test is considered positive when the biuret content exceeds 0.1% by weight.

The presence of biuret in the effluent indicates that the ion-exchanging resin 12 is exhausted. Therefore, a urea-recovering operation, as well as the operations of backwash, regeneration and rinse of the ion-exchanging resin 12 are necessary.

The urea-recovering operation comprises feeding water through line 15 to column 11 to displace the urea solution retained in the ion-exchanging resin 12. The liquid flowing through line 16 is a solution having a high urea content; therefore it can be reprocessed. When the concentration of the urea solution in the effluent flowing through line 16 drops to 3 or 4% by weight the said solution is considered as not being useful and this operation is concluded.

After the above operation, the backwash is performed. That is, the water flow is inverted by passing it through lower line 17 and flowing out through upper line 17. When the backwash has been established, the rate of flow is increased for eliminating suspended solids and for raising the ion-exchanging resin 12; this situation is kept for a certain interval of time in order to appropriately clean the resin 12.

After the backwash operation, the regeneration is initiated which, in this case will be carried out using caustic soda having a concentration of 15 to 45% by weight. For this operation, the remaining water from the backwash operation, that necessarily entirely covers the resin 12, is drained until reaching just above the level of the said resin 12; then the feeding of caustic soda is started through line 15. In this manner, the water contained in the ion-exchanging resin 12 is displaced, flowing out through line 16. The first amount of outflowing liquid is eliminated since this represents the last backwash water, until the outflowing liquid reaches a concentration of about 3% by weight of caustic soda. Once this concentration is reached, the effluent liquid is recovered, and the regeneration operation is maintained for a time according to the type of ion-exchange resin 12 embedded in column 11.

After the above procedure, it can be considered that the ion-exchanging resin 12 has been regenerated. But, it is necessary to recover the caustic soda still contained in the said ion-exchanging resin 12 and this is carried out by a water displacement that is continued until the effluent through line 16 has a caustic soda concentration of 3% by weight. After this time, the effluent liquid is discarded and the introduction of water is continued with an increased flow rate. This operation is considered as a rinse operation and it is ended when the effluent contains 500 p.p.m. of caustic soda. In this manner, the ion-exchanging resin 12 is ready for a new operating cycle.

As can be seen from the above, with this type of ion-exchanger, the process represents a batch process since the recovery, backwash, regeneration and rinse operations are required. If a continuous operation is desired, it will be necessary to have duplicate ion-exchanging columns so that, while in one of them the urea solution is processed in the other the several different operations can be performed.

Another possible embodiment of the process of the present invention can be carried out (see Figure 2) by means of a continuous ion-exchange system. In this system three columns 21, 22 and 23 are located in such a manner that column 21 is connected at its lower end to column 22 by means of line 24, including its valve 25; besides the said column 22 is connected at its lower end to column 23 by means of line 26, also including its valve 27; and that column 23 is connected at its lower end to column 21 through line 28 including valve 29, with which a continuous recycling system is obtained.

Moreover, each column 21, 22 and 23 comprises at its lower end, feeding inlets 30, 31 and 32 respectively through which, by means of pumps 33, 34 and 35, respectively the corresponding liquids to be fed to each column 21, 22 and 23 are introduced. Likewise, at its

upper ends, columns 21, 22 and 23 include outlet lines 36, 37 and 38 respectively, through which the liquids fed to each column 21, 22 and 23 respectively flow out.

- 5 In this type of apparatus, column 21 contains a certain amount of an ion-exchanging resin 39, which can be of the same type as in the case of the batch operation previously described, that is, a strongly basic styrene resin.
- 10 Then, through inlet 30 a urea solution containing biuret is pumped for contacting the ion-exchange resin 39 whereby, through line 36, a biuret free urea is obtained. The pumping operation is thus continued until it is considered that a sufficient amount of resin 39, although not all, has been exhausted. This
- 15 interval of time will be taken as a standard for further operating cycles.

- 20 After the selected period has elapsed, a certain amount of exhausted resin 39 is transferred from column 21 to column 22; allowing at the same time for a corresponding amount of a regenerated resin 40, embedded in column 23, to be transferred to column 21 to keep the total volume of resin in the column
- 25 21 constant.

- 30 Regeneration of exhausted resin 39 in column 22 is carried out using caustic soda. The caustic soda is pumped through inlet 31 and flows out through inlet line 37 keeping a flow during a suitable period for regenerating exhausted resin 39.

- 35 After the resin 39 has been regenerated, it is passed through line 26 to column 23 wherein it is subjected to a rinse operation. This rinse operation is carried out by introducing water into the column 23, through inlet 32 and by using pump 35 and allowing the water to flow out through line 38. The water flow is continued during the time necessary for displacing almost all the caustic soda retained in the resin 39. In this manner, a washed and regenerated resin 40 is provided, that is ready for re-use in column 21, as previously indicated.

- 40 The above-mentioned systems may be adapted or included in urea-synthesis plants for obtaining an end product with a very low biuret content. The location of the ion-exchange systems in the urea-synthesis plants is not critical, even in intermediate steps, provided the required final biuret content in the
- 45 urea is taken into account.
- 50

The efficiency of the process of the present invention is illustrated by the following examples in which there were used various ion-exchanging resins and urea solutions prepared from non-coated prilled urea.

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## LABORATORY EXAMPLES

### EXAMPLE 1.

A number of different tests were carried out, by treating a 50% by weight urea solution containing 1.09% by weight of biuret on dry urea basis, at various temperatures with 200 millilitres of activated carbon as an ion-exchanger. The obtained results are shown in Table I.

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### EXAMPLE 2.

A 50% by weight urea solution containing 1.17% by weight of biuret on dry urea basis, was treated with 150 millilitres of a cationic resin "Amberlite" IR-120. The obtained results are shown in Table II. "Amberlite" is a Trade Mark.

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### EXAMPLE 3.

Tests were carried out treating a 50% by weight urea solution containing 1.17% by weight of biuret on dry urea basis, with 150 millilitres of a weak anionic resin IRA-93. The obtained results are shown in Table III.

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### EXAMPLE 4.

Several tests were carried out treating a 50% by weight urea solution containing 1.12% by weight of biuret on dry urea basis, with 200 millilitres of a strong anionic resin SBR-P. The obtained results are shown in Table IV.

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### EXAMPLE 5.

A 50% by weight urea solution containing 1.15% by weight of biuret on dry urea basis was treated with 200 millilitres of an extra strong anionic resin "IONAC-935". The results obtained in this example did not indicate the presence of biuret until 1600 millilitres of the urea solution had passed through the bed. That is, during the passage of the above-mentioned millilitres up to this value, the percentage of biuret on a dry urea basis in the effluent is considered to be 0%.

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TABLE I

RUN I						
T = 20°C						
Ml. of urea solution passed through the bed	100	200	300	400	500	600
% by weight of biuret on dry urea basis, in the effluent	0.22	0.22	0.35	0.53	0.70	0.93
Run II						
T = 60°C						
Ml. of urea solution passed through the bed	100	200	300			
% by weight of biuret on dry urea basis, in the effluent	0.15	0.46	0.46			
RUN III						
T = 75°C						
Ml. of urea solution passed through the bed	100	200	300	400		
% by weight of biuret on dry urea basis, in the effluent	0.30	0.40	0.56	0.80		

TABLE II

Ml. of urea solution passed through the bed	100	200	300	400	500
% by weight of biuret on dry urea basis, in the effluent	0.69	0.95	1.07	1.11	1.16
Regeneration	With a 4% by weight hydrochloric acid solution and a regeneration level of 9 lbs. HCl/ft <sup>3</sup> of resin.				

TABLE III

RUN I	
Ml. of urea solution passed through the bed	100
% by weight of biuret on dry urea basis, in the effluent	0.62
Regeneration	With a 4% by weight caustic soda solution and a regenerating level of 5 lbs NaOH/ft <sup>3</sup> of resin.

TABLE III (Continued)

RUN 2	
Ml. of urea solution passed through the bed	100      200
% by weight of biuret on dry urea basis, in the effluent	0.11      0.77
Regeneration	With a 4% by weight caustic soda solution and a regeneration level of 5 lbs. of NaOH/ft <sup>3</sup> of resin.
Note: Ammonia and sodium hydroxide were added until the pH was 13.4 at which time the biuret is subject to complex.	



TABLE IV

RUN I									
Ml. of urea solution passed through the bed	100	200	300	400	500	600	700	800	900
% by weight of biuret on dry urea basis, in the effluent	0.05	0.08	0.08	0.08	0.08	0.08	0.09	0.10	0.10
Regeneration	With a 4% by weight caustic soda solution and a regeneration level of 5 lbs. NaOH/ft <sup>3</sup> of resin.								
RUN II									
Ml. of urea solution passed through the bed	100	200	300	400	500	600	700	800	1000
% by weight of biuret on dry urea basis, in the effluent	0.25	0.36	0.36	0.36	0.35	0.35	0.36	0.46	0.74
Regeneration	With a 4% by weight ammonia solution and a regeneration level of 5 lbs. NH <sub>3</sub> /ft <sup>3</sup> of resin.								

TABLE IV (Continued)

RUN 3										
Ml. of urea solution passed through the bed	100	200	300	400	500	600	700	800	900	1000
% by weight of biuret on dry urea basis, in the effluent	0.18	0.25	0.26	0.32	0.38	0.52	0.76	0.91	1.01	1.07
Regeneration	With a 4% by weight ammonia solution and a regeneration level of 10 lbs NH <sub>3</sub> ft <sup>3</sup> of resin.									
RUN 4										
Ml. of urea solution passed through the bed	100	200	300	400	500	600	700	800	900	
% by weight if biuret on dry urea basis, in the effluent	0.11	0.11	0.09	0.08	0.08	0.08	0.09	0.08	0.10	
Regeneration	With a 4% by weight caustic soda solution and a 4% by weight ammonia solution, and with regeneration levels respectively of 2.5 lbs. NaOH/ft <sup>3</sup> of resin and 5 lbs. NH <sub>3</sub> /ft <sup>3</sup> of resin.									

## PILOT PLANT EXAMPLE

From laboratory examples it was determined that the resin providing the best results is as "IONAC"—935. Therefore, in a pilot plant, the runs were only carried out with extra-strong anionic resin "IONAC"—935. The results obtained are shown in Table A.

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TABLE A

Run	Capacity Kg Biuret M <sup>3</sup> resin	Treated Urea Solution			Final Biuret %	
		Vol. M <sup>3</sup>	Concentration % by wt. Urea Biuret	Operating temperature, °C		
1	30.38	1.40	62.5	1.88	57	0
2	31.55	1.45	62.5	1.88	57	0
3	32.50	1.50	62.5	1.88	57	0
4	32.45	2.7	58.5	0.89	55	0
5	42.4	2.3	56.5	1.36	38	0
6	49.07	3.25	54.5	1.12	40	0
7	29.19	2.1	66	1.01	56	0
8	34.55	4.6	51	0.56	26	0
9	27.25	3.7	55	0.55	29	0

## WHAT WE CLAIM IS:—

1. A process for treating a urea melt or urea solution containing 1.0 to 99.9% by weight of urea and an amount of biuret itself or a metal complex thereof to reduce the amount of biuret or complex thereof which comprises contacting the urea melt or solution with an ion-exchanging resin.
2. A process as claimed in Claim 1, wherein an aqueous urea solution is treated with the ion-exchanging resin.
3. A process as claimed in Claim 1 or Claim 2, wherein the ion-exchanging resin is a strongly basic anionic resin.
4. A process as claimed in a preceding claim, which is conducted at a temperature of 0°C to 200°C.
5. A process as claimed in any preceding

claim, which is conducted by batch ion-exchange.

6. A process as claimed in any one of Claims 1 to 4, which is conducted by continuous ion-exchange.

7. A process as claimed in Claim 1 substantially as herein described with particular reference to the accompanying drawings or to any one of the examples.

8. A urea melt or urea solution which has been produced by the process claimed in any preceding claim.

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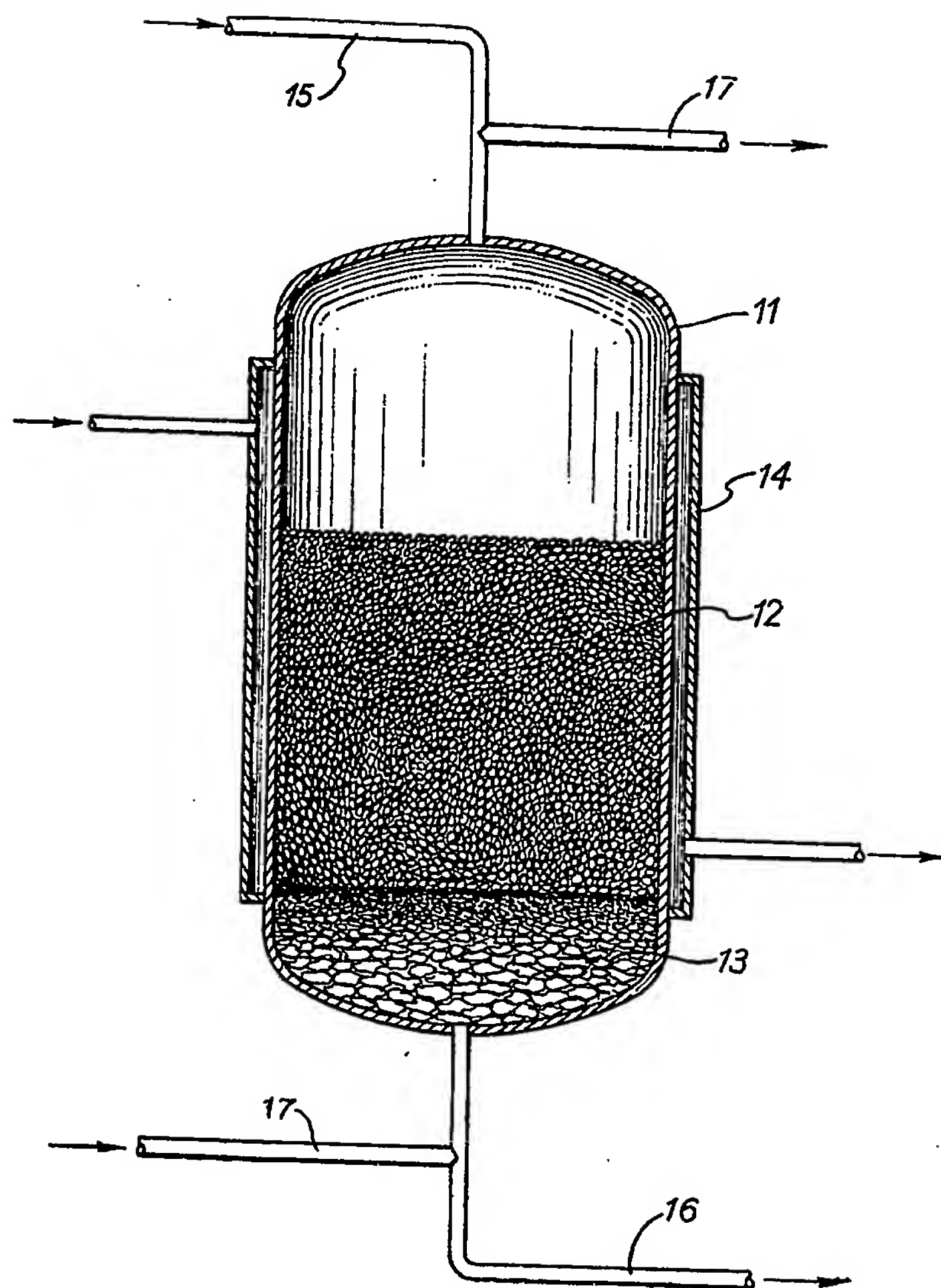


Fig. 1.



